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## PRIORITY DOCUMENT

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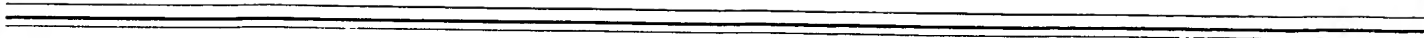
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Dated 14 September 2000



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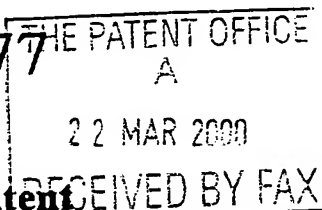
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# Patents Form 1/77



The Patent Office  
Cardiff Road  
Newport  
NP9 1RH

## Request for grant of a patent

1. Your Reference

APB/MER/S82

2. Application number

0006884.1

22 MAR 2000

3. Full name, address and postcode of the or each Applicant

Country/state of incorporation (if applicable)

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4. Title of the invention

ION EXCHANGE POLYMERS

5. Name of agent

APLEYARD LEES

Address for service in the UK to which all correspondence should be sent

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HX1 2HY

Patents ADP number

190001

6. Priority claimed to:

Country

Application number

Date of filing

7. Divisional status claimed from:

Number of parent application

Date of filing

8. Is a statement of inventorship and of right to grant a patent required in support of this application?

YES

Patents Form 1/77

Page 2/2

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item

Priority documents

Translation of priority documents

Statement of inventorship and right to grant a patent (PF 7/77)

Request for a preliminary examination and search (PF 9/77)

Request for substantive examination (PF 10/77)

Any other documents (please specify)

11.

We request the grant of a patent on the basis of this application.  
Signature Date

APPLEYARD LEES

22 March 2000

12. Contact

Anthony P Brierley- 01422 330110

COMPOSITE ION-EXCHANGE MEMBRANES CASE 1

This invention relates to a composite ion-exchange membrane and provides such a membrane per se and a method  
5 of making such a membrane.

One type of known polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin  
10 sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

15

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:

20 Pt-Anode (Fuel Electrode)  $2H_2 \rightarrow 4H^+ + 4e^-$

The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following  
25 electrochemical reaction takes place:

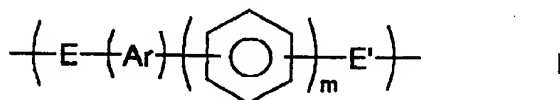
Pt-Cathode (Oxidant Electrode)  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Thus, electrons and protons are consumed to produce  
30 water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

The PEM 2 could comprise a single layer of ion-conducting material. However, in many cases, a single layer of material does not have satisfactory mechanical  
5 properties.

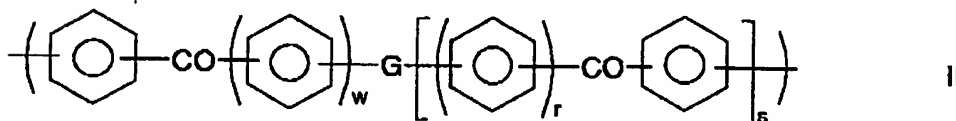
It is an object of the present invention to address the above described problem.

10 According to a first aspect of the invention, there is provided a composite membrane which includes a conductive polymer and a support material for the polymer, said polymer having a moiety of formula



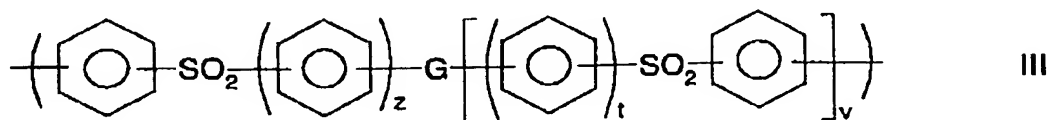
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and/or a moiety of formula



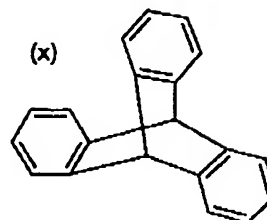
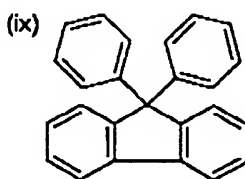
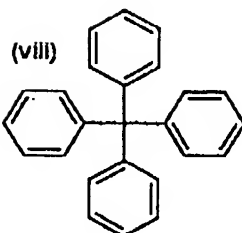
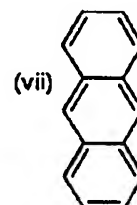
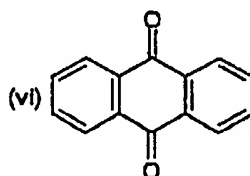
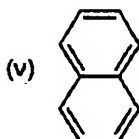
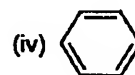
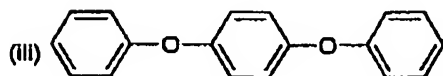
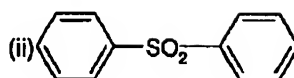
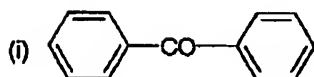
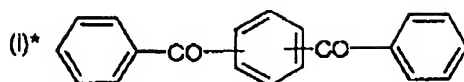
and/or a moiety of formula

20



wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and  
5 wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from  
10 one of the following moieties <sup>(v\*)</sup>(i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

4



5

Preferably, said conductive polymer and said support material do not, together, define a homogenous mixture.

10 Suitably, to provide said ion exchange sites, said polymer is sulphonated, phosphorylated, carboxylated,



quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield  $-\text{CH}_2\text{PO}_3\text{H}_2$ ,  $-\text{CH}_2\text{NR}_3^{20+}$  where  $\text{R}^{20}$  is an alkyl, or  $-\text{CH}_2\text{NAr}_3^{x+}$  where  $\text{Ar}^x$  is an aromatic (arene), to provide a cation or anion exchange membrane.

- 5 Further still, the aromatic moiety may contain a hydroxyl group which can be readily elaborated by existing methods to generate  $-\text{OSO}_3\text{H}$  and  $-\text{OPO}_3\text{H}_2$  cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

10

Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

15

- References to sulphonation include a reference to substitution with a group  $-\text{SO}_3\text{M}$  wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H,  $\text{NR}_4^{y+}$ , in which  $\text{R}^y$  stands for H,  $\text{C}_1\text{-C}_4$  alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H,  $\text{NR}_4^+$ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

25

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

30

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C<sub>1-10</sub>, especially C<sub>1-4</sub>, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens, C<sub>y</sub>F<sub>2y+1</sub> where y is an integer greater than zero, O-R<sup>q</sup> (where R<sup>q</sup> is selected from the group consisting of alkyls, perfluoralkyls and aryls), CF=CF<sub>2</sub>, CN, NO<sub>2</sub> and OH. Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be

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effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described  
5 in EP-A-0008895.

However, for polymers according to the invention described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a  
10 material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

15

Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene  
20 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

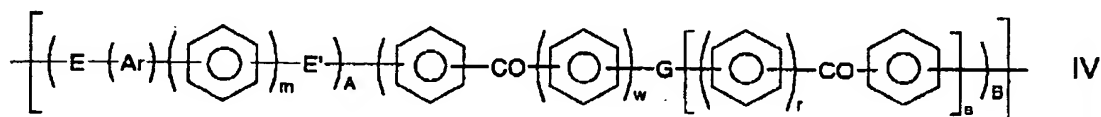
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Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;  
30 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52.

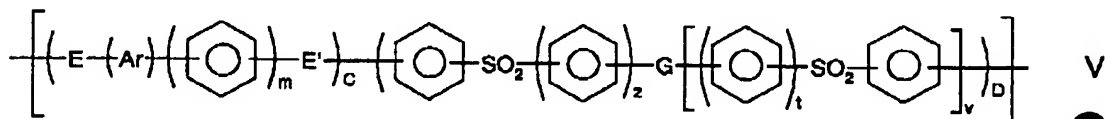
Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1.

- 5 Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about 100. Preferably, said polymer consists essentially of moieties I, II and/or III.

- 10 Said polymer may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



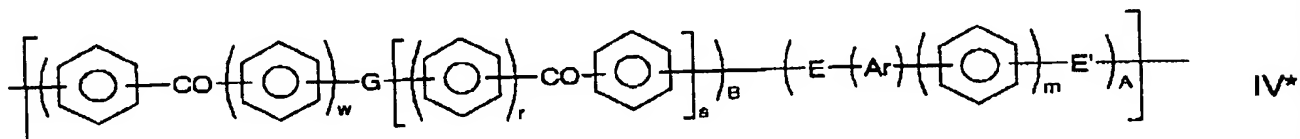
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or a random or block copolymer of at least two different units of IV and/or V

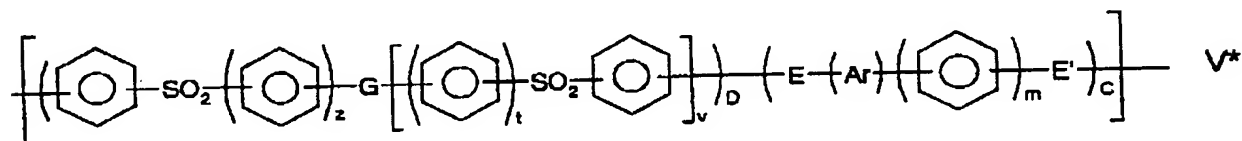
- wherein A, B, C and D independently represent 0 or 1  
20 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

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As an alternative to a polymer comprising units IV and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula



5 or a homopolymer having a repeat unit of general formula



10 or a random or block copolymer of at least two different units of IV\* and/or V\*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

15 Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

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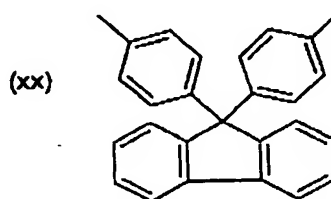
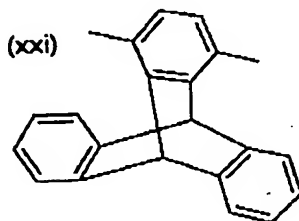
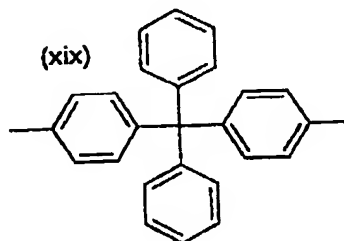
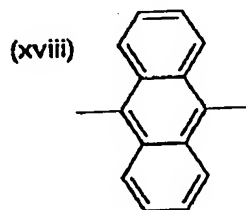
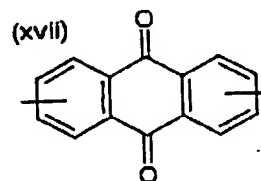
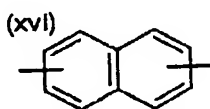
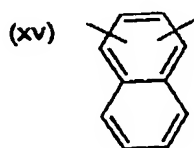
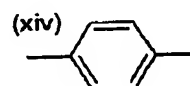
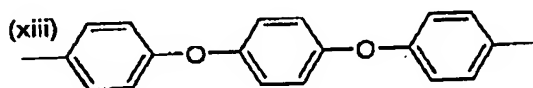
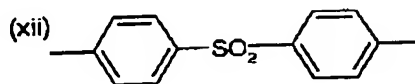
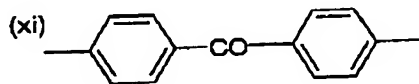
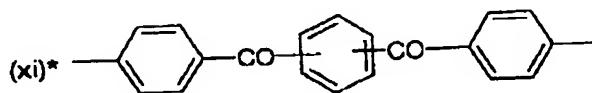
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Preferably Ar is selected from the following moieties  
(xi)\*, (xi) to (xxi):

11



Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

One preferred class of polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO<sub>2</sub>- moieties between aryl (or other unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second

aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said



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homopolymer or copolymer suitably includes a repeat unit of general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

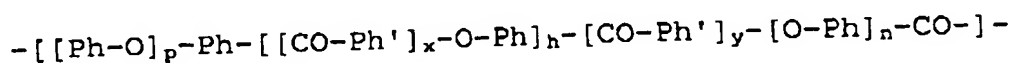
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Referring to formula IV, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, G represents a direct link and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

20

Referring to formula V, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

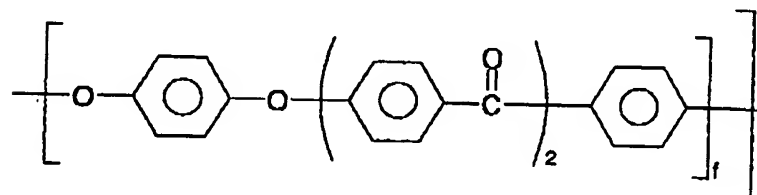
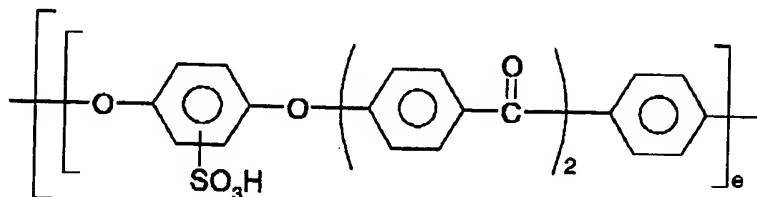
Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula



where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

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Preferably, said polymer does not conform to the formula



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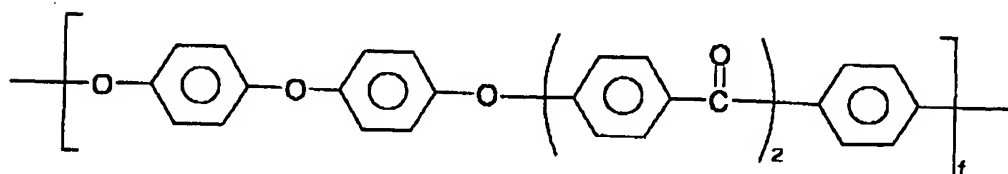
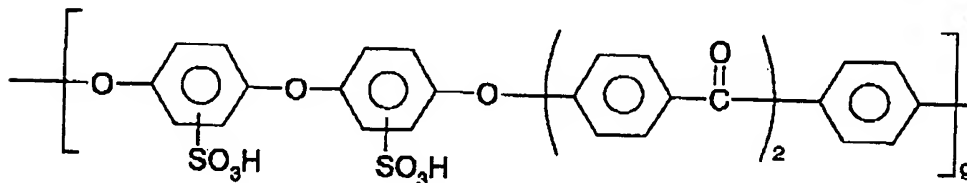
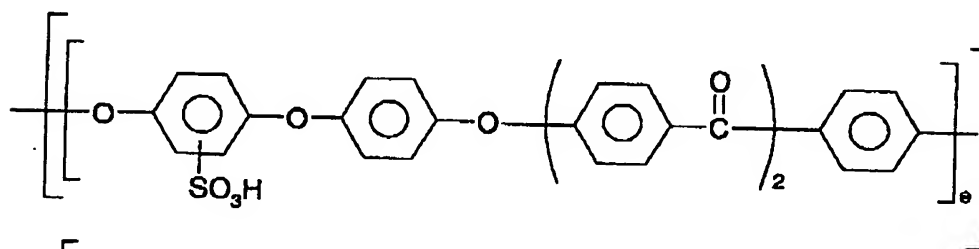
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

e + f = 1

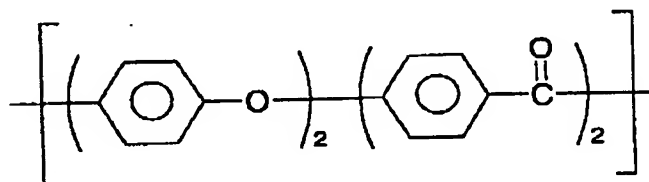
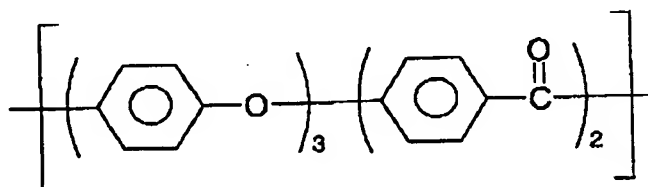
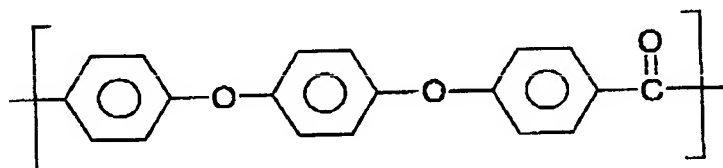
Preferably, said polymer does not conform to the  
10 formula



15

in which e is a number from 0 to 1, g is a number from 0 to 1, f is a number from 0 to 0.5, and the sum  $e + f + g = 1$ .

- 5 Preferably, said polymer is not a copolymer built up from at least two different units of formulae:



~~from at least two different units of formulae:~~

- 10 Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In  
15 relation, in particular to the alternative polymers comprising units IV\* and/or V\*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be  
5 sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least  $10\pi$  electrons in a delocalized aromatic moiety. The number of  $\pi$  electrons may be 12 or less. Preferred polymers include a biphenylene moiety. Other  
10 preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms. Especially preferred polymers include a -O-biphenylene-O-moiety. Other especially preferred polymers include a -O-  
15 naphthalene-O- moiety.

Preferred polymers include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For  
20 example, said second moiety may be sulphonatable using the relatively mild method described in Example 2 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 2 may be advantageous over currently used methods  
25 which use oleum. A preferred second said moiety includes a moiety  $-\text{Ph}_n-$  wherein  $n$  is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen. Especially preferred is the case wherein said moiety is  $-\text{O}-\text{Ph}_n-\text{O}-$  where said ether groups are para to the Ph-Ph bond.

30

Preferred polymers are copolymers comprising a first repeat unit which is selected from the following:

17

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

5

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

10

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

15

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

20

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

25

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

30

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

5

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

10

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

15

Other second units which may form copolymers with any of said first repeat units (a) to (e) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

20

Preferred polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred.

25

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially

30

repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Preferred polymers having repeat unit(s) of formulae  
5 IV\* and V\* may include: a unit of formula IV\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a  
10 repeat unit of formula V\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

Said polymers having repeat units IV\* and V\* may  
15 include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV\* may be preferred.

20 Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and  
25 second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

30

Preferred polymers suitably have a solubility of at least 10% w/v, preferably a solubility in the range 10 to 30 %w/v in a polar aprotic solvent, for example NMP, DMSO

or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily -O-(phenyl)<sub>n</sub>-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)<sub>n</sub>-CO- or -O-(phenyl)<sub>n</sub>-SO<sub>2</sub>- may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae -CO-(phenyl)<sub>n</sub>-CO- and -SO<sub>2</sub>-(phenyl)<sub>n</sub>-SO<sub>2</sub>- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

The glass transition temperature (T<sub>g</sub>) of said polymer may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T<sub>g</sub> may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.



Said polymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm<sup>-3</sup>, said solution containing 1g of polymer per 100cm<sup>3</sup> of solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm<sup>3</sup>, said solution containing 0.1g of polymer per 100cm<sup>3</sup> of solution.

The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm (T<sub>m</sub>) for said polymer (if crystalline) may be at least 300°C.

In general terms, said composite membrane is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5µm.

Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least 5 $\mu$ m and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

Said support material suitably imports mechanical strength and dimensional stability to the composite membrane. The polymer may be associated with the support material to form a composite membrane in a variety of ways. For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be impregnated into the support material. Said support material may comprise or consist essentially of an optionally-substituted polyolefin. Preferred polyolefins are optionally-substituted polyethylene and polypropylene. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene or surface modified polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

Said support material may be made of any polymer described herein for said conductive polymer except that

the polymer of said support material is either not sulphonated or otherwise functionalized to provide ion-exchange sites or is only sulphonated (or otherwise functionalized to provide ion-exchange sites) at or in the region of the surface of the support material - that is, functionalisation of said support material is greater at the surface than in interior regions thereof. The EW of said support material may be greater than 2000. Thus, said support material may comprise a polymer having moieties I, II and/or III or a homopolymer or copolymer comprising units IV and/or V.

Preferably said support material is selected from the following homopolymers of formula IV:

15

- E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1

20 - E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero

25 - Ar represents a moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

30 - Ar represents a structure (i)\*, E represents an oxygen atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.

24

- Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1

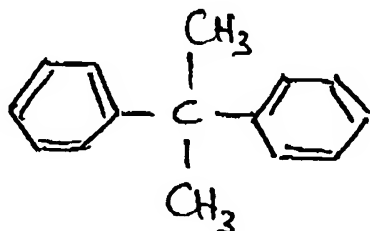
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- Ar represent moiety (iv), E represents a sulphur atom, m represents 0, E' represents a direct link and B represents 0 and is selected from:

- 10 - a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:

- 15 - polysulphone for example comprising a homopolymer of formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

20



25

- 30 ~~[Phenyl - C(CH<sub>3</sub>)<sub>2</sub> - Phenyl - 1]~~

Blends of the abovementioned materials may be used.

25

Said support material may be any support material described in WO99/10165 the content of which is incorporated herein, as regards said support materials.

5

Said support material is preferably impregnated with said conductive polymer. Said support material is preferably porous and, suitably, said conductive polymer is arranged in pores of said support material, preferably so as to render an interior volume of the support material substantially occlusive.

A said porous support material may be provided by a fabric which may have warp and weft strands or may comprise an irregular arrangement of fibres. Suitably, said pores are defined by the void volume of the fabric - that is between the fibres. However, the fibres of the fabric themselves may be porous and penetrated by said conductive polymer. Alternatively, a said porous support material may be microporous and may suitably be made by a phase inversion process as hereinafter described. Such a microporous material preferably has no through pores and/or contains no closed pores.

25 Preferably, said support material and said conductive polymer are in intimate contact. Whilst the two materials preferably do not together define a homogeneous material, the support material and conductive polymer preferably intermingle (as would happen if, for example a surface of the support material was dissolved and contacted with said conductive material) in a boundary region between the two materials.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 500 g/mol, less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used as said conductive polymer is said composite membrane.

The composite membrane suitably includes a catalyst material (preferably a layer of a catalyst material) which is suitably a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of the support material/conductive polymer arrangement described. Electrodes may be provided outside the catalyst material.

It may be preferable for each phenyl group in a conductive polymer (e.g. a sulphonated polymer) as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

According to a second aspect of the invention, there is provided a composite membrane which includes a conductive polymer and a support material for the polymer, wherein said polymer includes: polyaryletherketone and/or polyarylethersulphone units; and units of formula  $-O-Ph_n-O-$  (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

Preferably, each phenyl group of moiety  $Ph_n$  is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably, -OPhCO- and/or -OPhSO<sub>2</sub>- moieties of said polymer are sulphonated to a lesser extent than the phenyl groups of moiety Ph<sub>n</sub>. Moieties -OPhCO- and -OPhSO<sub>2</sub>- may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said polymer electrolyte membrane may be for a fuel cell or an electrolyser.

The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a conductive polymer for a composite membrane as described herein.

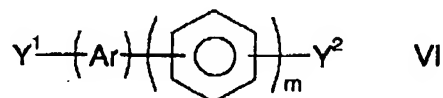
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The conductive polymer described herein may include a blend of polymers, at least one of which is a polymer described according to the invention described herein. Suitably the conductive polymers herein are blended with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric materials. Preferably, however, a blend of polymers is not provided.

According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects. The fuel cell may be a hydrogen or direct methanol fuel cell.

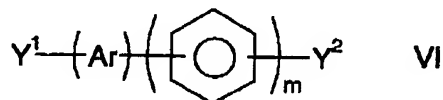
Polymers having units I, II, III, IV, IV\*, V and/or V\* may be prepared by:

- 5 (a) polycondensing a compound of general formula



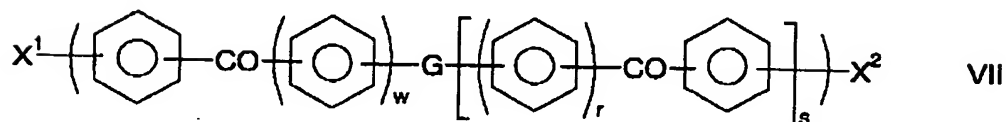
with itself wherein  $Y^1$  represents a halogen atom or a group -EH and  $Y^2$  represents a halogen atom or, if  $Y^1$  represents a halogen atom,  $Y^2$  represents a group E'H; or

- (b) polycondensing a compound of general formula



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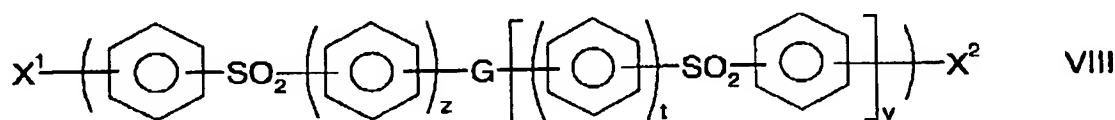
with a compound of formula



20

and/or with a compound of formula





5        wherein  $Y^1$  represents a halogen atom or a group -EH (or  
 -E'H if appropriate) and  $X^1$  represents the other one of a  
 halogen atom or group -EH (or -E'H if appropriate) and  $Y^2$   
 represents a halogen atom or a group -E'H and  $X^2$  represents  
 the other one of a halogen atom or a group -E'H (or -EH if  
 10 appropriate).

(c) optionally copolymerizing a product of a process as  
 described in paragraph (a) with a product of a process as  
 described in paragraph (b);

15

wherein the phenyl moieties of units VI, VII and/or  
 VIII are optionally substituted; the compounds VI, VII  
 and/or VIII are optionally sulphonated; and Ar, m, w, r, s,  
 z, t, v, G, E and E' are as described above except that E  
 20 and E' do not represent a direct link;

the process also optionally comprising sulphonating  
 and/or cross-linking a product of the reaction described in  
 paragraphs (a), (b) and/or (c) to prepare said polymer.

25

In some situations, the polymer prepared, more  
 particularly phenyl groups thereof, may be optionally  
 substituted with the groups hereinabove described after  
 polymer formation.

30

Preferably, where  $Y^1$ ,  $Y^2$ ,  $X^1$  and/or  $X^2$  represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

5

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

10

Wherein the process described in paragraph (a) is carried out, preferably one of  $Y^1$  and  $Y^2$  represents a fluorine atom and the other represents an hydroxy group. More preferably in this case,  $Y^1$  represents a fluorine atom and  $Y^2$  represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

15

When a process described in paragraph (b) is carried out, preferably,  $Y^1$  and  $Y^2$  each represent an hydroxy group. Preferably,  $X^1$  and  $X^2$  each represent a halogen atom, suitably the same halogen atom.

20

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull. Soc. Chem. Belg., 98 (9-10), 667 (1989).

25  
30

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be  
5 sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w. preferably at least 97%w/w, more preferably at least  
10 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours,  
15 more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

20

According to another aspect of the invention, there is provided a method of making a composite membrane as described herein, the method comprising causing a  
25 conductive polymer as described herein to be associated with a support material as described herein.

The conductive polymer may be associated with the support material in a variety of ways. The method may involve laminating conducting polymer and support material  
30 together. Preferably, however, the method involves impregnating porous support material with said conductive polymer.

Said porous support material may be a fabric or a microporous membrane.

Where said porous support material is a fabric, the  
5 method may include a step of contacting the fabric with a  
first solvent formulation comprising a first solvent and a  
conductive polymer, wherein the conductive polymer is  
preferably dissolved in the first solvent. Said fabric  
may, therefore, be impregnated with said formulation.  
10 Thereafter, said first solvent may be removed, leaving  
said conductive polymer in pores of said fabric.

Said first solvent and said porous support material  
may be selected so that said first solvent solubilises, to  
15 some degree, a surface of the support material. Said  
first solvent may be capable of dissolving the support  
material to a level of at least 5 wt%. This may improve  
contact between the conductive polymer and said support  
material. Optionally, said first solvent may be capable  
20 of functionalizing (e.g. sulphonating) said support  
material to provide ion-exchange site on a surface thereof  
as hereinbefore described.

Said first solvent may be a polar aprotic solvent, for  
25 example NMP, or may be a protic solvent. A polar aprotic  
solvent may not be capable of solubilising said porous  
support material whereas a protic solvent may be able to  
solubilize and, in some cases, functionalise (e.g.  
sulphonate) said porous support material.

30

Where said first solvent is a protic solvent, said  
solvent preferably comprises or consists essentially of a  
strong acid solvent. Said solvent may comprise at least

90%, preferably at least 95%, more preferably at least 97%, especially at least 98% acid. Said strong acid solvent may be one or more of sulphuric acid, a sulphonic acid (e.g. methane sulphonic acid, trichloromethane sulphonic acid, trifluoromethane sulphonic acid), hydrofluoric acid and phosphoric acid.

Preferably, a said protic first solvent comprises or consists essentially of sulphuric acid. Said solvent may include at least 96%, preferably at least 98% acid. Said solvent may include less than 99% acid. A said protic first solvent is preferably arranged to sulphonate easy to sulphonate units described herein, but not difficult to sulphonate units.

15

In one embodiment, said fabric may be PEEK<sup>™</sup> and this may be contacted with a formulation comprising the conductive polymer in sulphuric acid, whereby the sulphuric acid dissolves the surface of fibres of the PEEK<sup>™</sup> and sulphonates it and the conductive polymer penetrates pores defined between fibres of the fabric. Thereafter, phase inversion may be effected, suitably by contact with a non-solvent (e.g. water). After drying, the arrangement may be contacted with a formulation of the conductive polymer in a polar aprotic solvent which will not substantially attack the PEEK<sup>™</sup>, but may dissolve to some extent the conductive polymer already in the pores. In another embodiment, PEK<sup>™</sup> may be used in the process described instead of PEEK<sup>™</sup>. In this case, the PEK<sup>™</sup> is dissolved by the sulphuric acid, but not surface sulphonated. Otherwise the process is as described for the treatment of PEEK<sup>™</sup>.

Where said support is a microporous membrane, preparation of the membrane may include a step of contacting a support material as described herein with a solvent formulation comprising said first solvent. Said  
5 first solvent preferably solubilizes the support material.. Subsequently, the method preferably includes the step of contacting the support material with a second solvent. Said second solvent is preferably arranged to cause phase inversion. Phase inversion suitably results  
10 in said support material being rendered porous. Said second solvent is preferably a non-solvent for said support material. Preferred second solvents are aqueous; especially preferred is water.

15 Said microporous support material is preferably contacted with said conductive polymer so that said polymer penetrates into pores formed in said porous material. Said conductive polymer may be provided in said  
20 third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

Said third solvent may have the same identity as said  
25 first solvent described above. Said conductive material may be contacted with said support material in the first solvent. Phase inversion may then be caused as described above which results in said conductive polymer being deposited in the pores formed by the phase inversion.  
30 After deposition of said conductive polymer in pores, as described above, the arrangement may be post-treated, suitably so as to produce a substantially continuous film of said conductive polymer on the support material. Post-

35

treatment may include the step of contacting the composite membrane which comprises conductive polymer in pores of said support material with a third solvent in which said conductive polymer is relatively soluble and said support material is substantially insoluble. This may cause some dissolution of the conductive polymer in the pores resulting in film formation by coalescence of material between pores. Optionally, a said conductive polymer may be provided in said third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

The method may include a subsequent step of associating a catalyst material with the composite membrane prepared as described.

A said composite membrane described herein may be used in fuel cells or electrolyzers and, accordingly, the invention extends to a fuel cell or electrolyzer incorporating a composite membrane as described.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

The abbreviation NMP referred to means N-methylpyrrolidone.

PEEK™ and PEK™ are trade marks of Victrex Plc for  
5 polyetheretherketone and polyetherketone respectively.

A PEM 2 may comprise a layer of an ion-conducting material in combination with a layer of a reinforcing material, as described further below.

10

Example 1

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and  
15 outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (29.79g, 0.16 mole) 4,4'-dihydroxydiphenylsulphone (60.06g, 0.24 mole), and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen  
20 blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

25

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.6 kNsm<sup>-2</sup>; and a Tg of  
30 188°C.



Example 2

The polymer of Example 1 was sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general,  $^1\text{H}$  nmr in DMSO-d<sub>6</sub> confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit.

15

Example 3

The substrate, a piece of PEEK™ fabric having a thickness of 70µm and weight/unit area of  $1.7 \times 10^{-3} \text{g.cm}^{-2}$  was clamped in a 10 cm diameter circular frame and immersed in a 15% (w/w) solution of SPEDEK/PEKES(1:1:5) prepared in Example 2 in NMP. The wetted substrate was placed in vacuum oven at 105°C for 1.5 hrs to remove the NMP. The dry composite membrane was placed on a glass plate and a 50 µm thick wet coating of the solution of SPEDEK/PEKES prepared in Example 2 in NMP was applied with a Doctor Blade and dried in a vacuum oven at 105°C for 20 hrs to remove the NMP. The resulting composite membrane had a thickness of 70 µm. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

30

#### Example 4

The substrate, a 150 cm by 130 cm piece of PEEK™ fabric as described in Example 3 was clamped to a glass plate, impregnated with a 10% (w/w) solution of the SPEDEK/PEKES prepared in Example 2 in 98% sulphuric acid and immediately immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP, to 100 µm wet thickness and dried. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

#### Example 5

The procedure described in Example 4 was followed except that instead of coating with SPEDEK/PEKES in NMP, the composite membrane was coated with NMP alone, left for 30 minutes and dried. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite was strong and flexible.

#### Example 6

A 10% (w/w) solution of PEK™ (Grade P22, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.22 KN sm<sup>-2</sup>) in 98% sulphuric acid and was cast onto a glass plate to produce a 100 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This

membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250  $\mu$ m, followed by drying for 20 hours at 105 °C. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

#### Example 7

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A 10% (w/w) solution of PES was dissolved in 98% sulphuric acid and was cast onto a glass plate to produce a 100  $\mu$ m wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250  $\mu$ m, followed by drying for 20 hours at 105°C. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

#### Example 8

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The substrate, a 10 cm by 10 cm piece of PTFE fabric was clamped to a glass plate, impregnated with a 5% (w/w) solution of the SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w) and immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 5% (w/w) solution of SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w), to 250  $\mu$ m wet thickness and dried. The

coating procedure was repeated. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

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#### Example 9

A 7% (w/w) solution of Victrex @ PEEK™ (Grade 450G, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.45kNsm<sup>-2</sup>) in methanesulphonic acid was cast onto a glass plate to produce a 100 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 µm, followed by drying for 20 hours at 105 °C. The wet unreinforced membrane was highly swollen and fragile, whereas the wet composite membrane was strong and flexible.

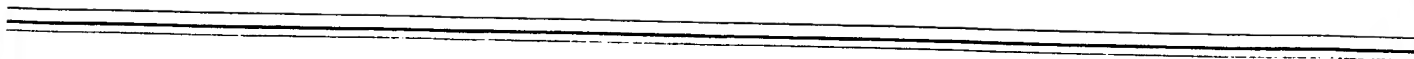
The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination,

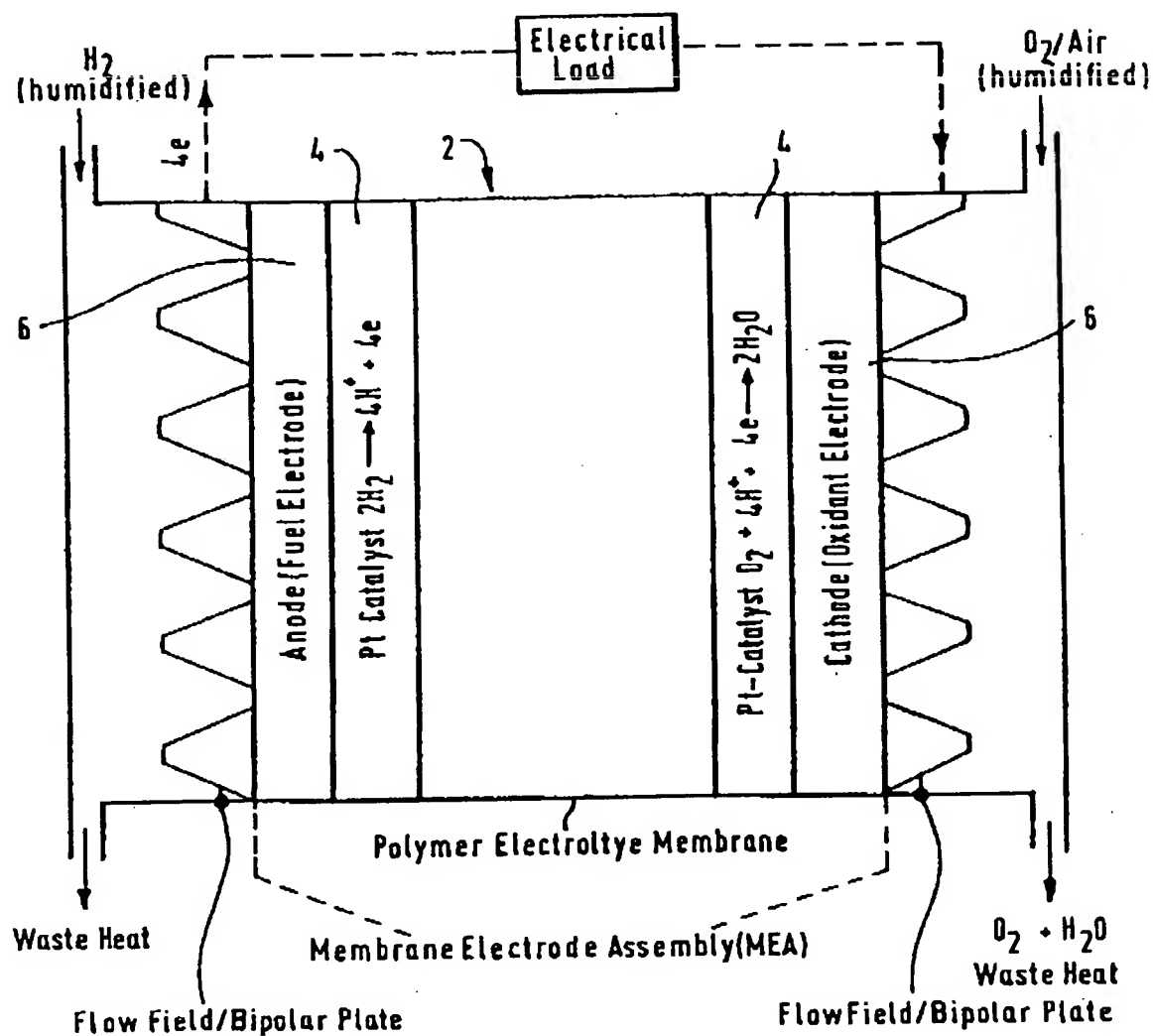
except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification  
5 (including any accompanying claims, abstract and  
drawings), may be replaced by alternative features serving  
the same, equivalent or similar purpose, unless expressly  
stated otherwise. Thus, unless expressly stated otherwise,  
each feature disclosed is one example only of a generic  
10 series of equivalent or similar features.

The invention is not restricted to the details of the  
foregoing embodiment(s). The invention extend to any novel  
one, or any novel combination, of the features disclosed  
15 in this specification (including any accompanying claims,  
abstract and drawings), or to any novel one, or any novel  
combination, of the steps of any method or process so  
disclosed.



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